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LOW TEMPERATURE SINTERABLE AND LOW LOSS DIELECTRIC CERAMIC COMPOSITIONS AND METHOD THEREOF

TECHNICAL FIELD

The present invention relates to a low temperature sinterable and low loss dielectric ceramic compositions for use in fabricating various high frequency devices such as a multilayer chip capacitor, a multilayer chip filter, a multilayer chip capacitor inductor composite device and module, a low temperature sinterable substrate, a resonator or a filter and a ceramic antenna, and its method.

BACKGROUND ART

Recently, with the rapid development in a mobile communication and a satellite communication, a high frequency dielectric ceramics is in a high demand as a material for a high frequency integrated circuit or a dielectric resonator.

Major characteristics of the dielectric ceramics used for a high frequency includes a high dielectric constant (ε_r), a quality factor (Q) and a stable and tunable temperature coefficient (τ_f) of a resonance frequency.

Representative high frequency dielectric compositions which have been widely known up to now are (Zr, Sn)TiO_4 group, BaO-TiO_2 group, (Mg, Ca)TiO_3 group, and Ba-($Zn_{1/3}Ta_{2/3}$)O_3, Ba($Mg_{1/3}Ta_{2/3}$)O_3, Ba($Zn_{1/3}Nb_{2/3}$)O_3 as Ba-peropskite group etc.

However, these compositions are disadvantages in that they are mostly

fired at a high temperature of 1,300~1,500°C, phase synthesis is not easy, a dielectric constant is low or a high-priced material should be used.

Besides, lately, advancement of a portable information communication devices lead to development of various types of substrates and multi-chip module (MCM) by a multilayer chip high frequency devices or low temperature co-firing ceramics (LTCC), and a research and development of a low temperature firing high performance high frequency ceramics are conducted accordingly.

However, there are problems that the performance of the high frequency characteristic is considerably degraded such as, for example, most of them are not sufficient in terms of density when being fired at a low temperature, a dielectric constant is decreased according to addition of a sintering aid, a quality factor is degraded and a temperature factor is changed.

In addition, silver or copper conduct with a small high frequency loss and a cofiring available low temperature firing high frequency dielectric ceramic are very rare.

Therefore, an object of the present invention is to provide a dielectric ceramics composition which can be fired at a very low temperature but has an excellent high frequency dielectric characteristic of various temperature compensation characteristics according to a high quality factor, a dielectric constant, a stable temperature factor and a composition, and can be implemented at a low cost.

Another object of the present invention is to provide a dielectric ceramics

composition which can employ Ag, Cu, their alloy or a Ag/Pd alloy as an internal electrode and thus be used for various high frequency devices, such as a multilayer chip capacitor, a multilayer chip filter, a multilayer chip capacitor/inductor composite device and a low temperature sinterable substrate, a resonator and a filter or a ceramic antenna.

DETAILED DESCRIPTION OF THE INVENTION

In order to achieve the above objects, there is provided a dielectric ceramics composition which is constructed by combining 1 mole of $(Zn_{1-x}M_x)TiO_3$ and $yTiO_2(0 \leq y \leq 0.6$ as a main component, one of 0~5 wt % B_2O_3, 0~5 wt % H_3BO_3, 0~5 wt % SiO_2-K_2O glass, 0~5 wt % B_2O_3 and SiO_2-K_2O glass, or 0~5 wt % H_3BO_3 and SiO_2-K_2O glass is added as an additive thereto, and fired at a low temperature of 800~925°C, its preparation method, and a high frequency dielectric ceramics device using the same. In this respect, 'M' is one of Mg, Co, Ni, 'x' is $0 \leq x \leq 0.55$ in case of Mg and 'x' is $0 \leq x \leq 1$ in case of Co, and $0 \leq x \leq 1$ in case of Ni

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graph showing a phase dissociation temperature of $(Zn_{1-x}M_x)TiO_3$ according to the substituted amount of Mg.

MODE FOR CARRYING OUT THE PREFERRED EMBODIMENTS

The present invention will now be described with reference to

accompanying drawings.

A high frequency dielectric ceramics composition of the present invention is characterized in that it has a very low firing temperature (800~925°C) compared to that of a conventional dielectric composition, has an excellent high frequency dielectric characteristic of various temperature compensation characteristics (τf = -52 ~ +104 ppm/°C) according to a high quality factor (Q x f = 12,000 ~ 84,000 GHz), a dielectric constant ($16 \le \varepsilon r \le 32$), a stable temperature factor and a composition, and can be implemented with a low-priced material such as ZnO, MgO, CoO, NiO, TiO_2,

In addition, the high frequency dielectric ceramics composition of the present invention is also characterized in that it employs Ag, Cu, their alloy or a Ag/Pd alloy as an internal electrode and thus be used for various high frequency devices, such as a multilayer chip capacitor, a multilayer chip filter, a multilayer chip capacitor/inductor composite device and a low temperature firing substrate, a resonator and a filter or a ceramic antenna.

In the present invention, the low temperature firing composition of the present invention has an excellent quality factor (close to the existing high temperature firing composition) more than several times the existing one. In addition, in the claimed composition coverage, combination of composition having an excellent high frequency characteristic of the almost infinite number can be obtained compared to any of the conventional ones.

$ZnTiO_3$ (crystal structure has a rhombohedral symmetry) is phase-dissociated to Zn_2TiO_4 (cubic symmetry) and TiO_2 (rutile) at a higher

temperature than 945°C (refer to Fig.303 of Phase Diagrams for Ceramist by the American Ceramic Society, System $ZnO-TiO_2$ by Dulin and Rase), and thus, it is very difficult to be prepared.

In order to obtain a pure $ZnTiO_3$, phase synthesis and firing must be made at a below 945°C. A preliminary experiment of the present invention shows a result through an X-ray diffraction analysis that phase dissociation starts at near 925°C so that a thermal treatment must be performed at below 925°C.

In a preferred embodiment of the present invention, in order to remove the shortcomings, Zn^{2+}, a positive ion of A-site constituting an ABO_3 type ilmenite phase ceramics, is substituted with Mg^{2+} (up to 0.55 mole), to thereby enlarge a thermal stabilization temperature of $ZnTiO_3$ to a high temperature range (refer to Figure 1), so that the preparation process coverage is widened and the high frequency dielectric characteristic are highly improved.

Figure 1 is a graph showing a phase dissociation temperature of $(Zn_{1-x} Mg_x)TiO_3$ according to the substituted amount of Mg. In case that a region x = 0, $ZnTiO_3$ is dissociated at a temperature of 945°C, and since the dissociation temperature goes up to a high temperature by the substitution of Mg, a single phase of the $(Zn_{1-x} Mg_x)TiO_3$ solid solution can be synthesized or fired even at a temperature of higher than 945°C.

Accordingly, a single phase can be obtained anywhere in the region II of Figure 1, which is the phase synthesis region of the present invention.

A high frequency dielectric ceramics composition in accordance with a

preferred embodiment of the present invention will now be described.

Powders (an average particle diameter is 1μm) of ZnO, MO (in this respect, MO is MgO, CoO or NiO) and TiO_2 (>99%) was weighed according to a composition range of $(Zn_{1-x}M_x)TiO_3$ and $yTiO_2$ (M is one of Mg, Co and Ni, x is $0 \leq x \leq 0.55$ in case of Mg, x is $0 \leq x \leq 1$ in case of Co, x is $0 \leq x \leq 1$ in case of Ni, and y is $0 \leq y \leq 0.6$), mixed in a wet ball mill method, dried at 120°C, and calcined and synthesized at a temperature of 850~950°C for four hours.

The calcined powder was mixed with 0.5 wt % B_2O_3, 0~5 wt % SiO_2-K_2O glass and a combination of 0~10 wt % B_2O_3 and SiO_2-K_2O as a sintering aid.

At this time, in case of B_2O_3, besides the oxide, a water soluble boron (H_3BO_3) was used to improve homogeneity in adding a little amount.

Solubility (per water 100cc) of boron to cool water (30°C) and hot water (100°C) is 6.35 and 27.6 (refer to Handbook of Chemistry and Physics, 55th ed., CRC Press, 1974-75).

In case of the present invention, cool water was used to make boron corresponding to the solubility to an aqueous solution, into which the main component or the main composition and the glass powder are mixed and crushed.

In crushing, since the temperature of slurry goes up further (especially, up to 45°C in case of high speed centrifugal crushing), the mixture of boron can be more uniform.

As for the SiO_2-K_2O glass, SiO_2 and K_2CO_3 were mixed with K_2CO_3 by 55~75 wt % and 25~45 wt %, melt at a temperature of 1100~1200°C, quenched

at cool deionized water, ball-milled for 24 hours, thereby obtaining glass powder, and it was confirmed that an amorphous phase of glass was obtained according to an X-ray diffraction analysis result.

Since the present invention is aimed at a low temperature firing at a below 925°C, in order to obtain fine powder (average particle diameter of below 0.5μm) less than submicron, a stabilized zirconia ball with a diameter of 2mm was used and crushed for four hours by an attrition mill, or a fine stabilized zirconia ball with a diameter of 1mm was used and subjected to a high speed centrifugal crushing for 5~10 minutes.

An aqueous solution to which 2 wt % PVA binder was added is mixed with the dried powder to make a granule of about 150μm and shaped to a disk test sample having a diameter of 8mm and a thickness of 3.8mm at a pressure of 98 Mpa.

The shaped test sample was maintained at a temperature of 300~500°C for over 3 hours to burn out the binder, and then sintered at a temperature 800~925°C at an atmosphere.

At this time, a heating rate was 10°C/min. The sintered test sample was ground with an SiC polishing paper (#1,500) to obtain about 0.45 ratio of diameter to thickness of the test sample.

The high frequency dielectric characteristic was measured in a $TE_{01\delta}$ mode by using a network analyzer (HP 8720C) by making a cylindrical dielectric ceramics resonator, and a dielectric constant was measure by a Hakki-Coleman method, a quality factor was measure by an open cavity method, a

temperature factor of a resonance frequency was measured by an invar cavity at a temperature range of +20~+70°C.

Table 1 shows a high frequency dielectric characteristic in case that B_2O_3, boron (H3BO3) and a combination component of boron and SiO_2-K_2O glass are added as sintering aids to a main composition that x=0.01 and y=0l2 among $(Zn_{1-x}M_x)TiO_3$ $(0\leq x\leq 0.55)$ and $yTiO_2$ $0\leq y\leq 0.6)$ composition.

In Table 1, a 800°C-sintered body had about more than 92% relative density, and 875°C-sintered body had about more than 97% relative density.

In the embodiments 2~5 and 6~10, it is noted that quality factor was further improved in case of adding boron instead of adding B_2O_3, and as for the temperature coefficient, the variation rate according to the sintering temperature (800°C and 875°C) was smaller. This effect results from a uniformity of boron.

As the sintering characteristic thanks to addition of B_2O_3, the dielectric constant and quality factor were much increased, and were increased up to about 2 wt % and then reduced at 5 wt %.

The temperature coefficient was moved to a positive as the amount of B_2O_3 is increased.

Accordingly, in the embodiments of Table 1, it is anticipated that if the value 'y' is a bit increased more than 0.2 and the amount of additive is controlled, an excellent dielectric property of which the temperature factor is almost '0' can be obtained.

That is, in order to be a usable high frequency characteristic, not only TiO_2, but the amount of additive needs to be controlled property, and

accordingly, various composition groups can be obtained.

Table 1: High frequency dielectric property of a dielectric resonator fabricated with composition of $(Zn_{00.99}M_{0.01})TiO_3$ (M=Mg) + $0.2TiO_2$ + (B_2O_3, H_3BO_3, or H_3BO_3 + SiO_2-K_2O glass)

No.	B_2O_3 (wt%)	H_2BO_3 (wt%)	SiO_2-K_2O glass (wt%)	Sintering temperat-ure (°C)	Dielectric constant (ε_r)	Quality factor (Qxf GHz)	Temperature coefficient (τf:ppm/°C)
1	-	-	-	800 875	13.8 21.1	22900 32400	-22 -50
2	0.25	-	-	800 875	22.3 26.9	65700 78200	-52 -48
3	0.50	-	-	800 875	23.0 26.4	54800 84600	-43 -40
4	1.00	-	-	800 875	19.7 26.5	50100 80900	-44 -33
5	2.00	-	-	800 875	19.6 27.2	44800 79300	-29 -22
6	-	0.25	-	800 875	22.1 27.0	59800 84300	-46 -43
7	-	0.50	-	800 875	20.2 26.0	50600 85200	-44 -39

8	-	1.00	-	800	19.3	47700	-33
				875	26.3	81200	-34
9	-	2.00	-	800	19.5	45400	-40
				875	26.7	70100	-20
10	-	5.00	-	800	16.5	40000	-10
				875	25.1	60200	+20
11	-	0.50	0.50	800	19.5	58800	-43
				875	25.8	67200	+39
12	-	0.50	1.00	800	17.0	42400	-20
				875	23.6	58400	-38
13	-	0.50	2.00	800	16.7	26300	-17
				875	23.8	45100	-36
14	-	0.50	3.00	800	15.4	25000	-21
				875	24.1	36200	-29
15	-	0.50	5.00	800	13.7	19100	-19
				875	23.4	24500	-43

Table 2 indicates a dielectric property in case of increasing the amount of Mg and TiO_2 (x = 0.55, Y = 0.6).

Table 2: High frequency dielectric property of a dielectric resonator fabricated with a composition of $(Zn0_{0.45}M_{0.55})TiO_3$ (M=Mg) + $0.6TiO_2$ + (B_2O_3, H_3BO_3, or H_3BO_3 + SiO_2-K_2O glass)

No.	B_2O_3 (wt%)	H_2BO_3 (wt%)	SiO_2-K_2O glass (wt%)	Sintering temperat-ure (°C)	Dielectric constant (ε_r)	Quality factor (Qxf GHz)	Temperature coefficient (τf:ppm/°C)
16	-	-	-	900	20.2	18300	+60
				925	24.3	20700	+56
17	0.25	-	-	900	26.9	19700	+54
				925	30.1	35300	+78
18	0.50	-	-	900	26.9	20300	+57
				925	29.5	44000	+65
19	1.00	-	-	900	26.0	22300	+51
				925	28.4	35300	+87
20	2.00	-	-	900	25.7	22400	+57
				925	28.6	30500	+79
21	-	0.25	-	900	27.3	23200	+72
				925	30.1	58900	+86
22	-	0.50	-	900	26.5	23000	+72
				925	29.3	46000	+70
23	-	1.00	-	900	25.3	23100	+55
				925	28.2	33400	+73
24	-	2.00	-	900	25.5	21700	+68
				925	28.1	27300	+88
25	-	5.00	-	900	23.7	21200	+75

				925	27.5	16600	+104
26	-	0.50	0.50	900 925	22.8 26.8	27900 22700	+54 +79
27	-	0.50	1.00	900 925	24.2 29.0	29800 26800	+46 +76
28	-	0.50	2.00	900 925	28.4 32.0	22300 17900	+65 +71
29	-	0.50	3.00	900 925	28.9 32.5	27600 19500	+49 +84
30	-	0.50	5.00	900 925		21200 11900	+33 +53

In the above embodiments, positive temperature coefficients were obtained. In this case, a temperature coefficient of '0' can be naturally obtained by adequately reducing the amount of TiO_2.

Meanwhile, in case that $x > 0.55$, the dielectric constant and the quality factor were much degraded than those of the present invention, and most of all, the sintering characteristic is degraded as the amount of Mg is increased.

Table 3 indicates a composition exhibiting an excellent dielectric property with a temperature coefficient of '0' on the basis of Table 1 and Table 2.

Table 3: High frequency dielectric property of a dielectric resonator fabricated with a composition of $(Zn0_{0.70}M_{0.30})TiO_3$ (M=Mg) + $0.2TiO_2$ + (B_2O_3, + SiO_2-K_2O glass)

No.	B_2O_3 (wt%)	SiO_2-K_2O glass (wt%)	Sintering temperat-ure (°C)	Dielectric constant (ε_r)	Quality factor (Qxf GHz)	Temperature coefficient (τf:ppm/°C)
31	-	0.50	925	16.6	26900	-16
32	0.25			24.5	65300	-11
33	0.50			24.9	69700	-6
34	1.00			24.7	74700	-10
35	1.50			24.4	69000	-1
36	2.00			24.2	67300	-5
37	-	1.00	925	17.1	27200	-27
38	0.25			24.8	58500	-14
39	0.50			25.0	59200	-7
40	1.00			25.0	59300	-2
41	1.59			24.7	55400	0
42	2.00			24.5	55800	+1
43	-	2.00	925	18.3	20300	-14
44	0.25			25.1	52200	-9
45	0.50			25.2	52700	-4
46	1.00			25.0	55700	+5
47	1.50			25.3	48100	+2
48	2.00			24.9	50800	+14

No.	B_2O_3 (wt%)	SiO_2-K_2O glass (wt%)	Sintering temperat-ure (°C)	Dielectric constant (ε_r)	Quality factor (Qxf GHz)	Temperature coefficient (τf:ppm/°C)
49	-	3.00	900	17.6	25400	-24
50	0.25			21.9	33600	-20
51	0.50			23.8	39100	-10
52	1.00			25.6	38400	+17
53	1.50			25.6	44800	+20
54	2.00			25.5	42100	+26
55	-	5.00	900	19.5	19500	-17
56	0.25			21.8	27100	-20
57	0.50			22.8	30700	-32
58	1.00			23.9	31600	-11
59	1.50			25.0	36800	+24
60	2.00			25.1	37700	+31

In the embodiments 32~60, an excellent dielectric property with a dielectric constant of more than 24, a quality factor of more than 50000 and a temperature factor of ± 30ppm/°C was obtained from the combination of less than 2 wt % B_2O_3 (or H_3BO_3) and SiO_2-K_2O glass.

Table 4 shows an influence of B2O3 and H3BO3 additive for the composition of $(Zn_{0.70}Mg_{0.30})TiO_3$ and $0.2TiO_2$.

Table 4: High frequency dielectric property of a dielectric resonator fabricated with a composition of $(Zn0_{0.70}M_{0.30})TiO_3$ (M=Mg) + $0.2TiO_2$ + (B_2O_3, or H_3BO_3)

No.	B_2O_3 (wt%)	H_2BO_3 (wt%)	Sintering temperature (°C)	Dielectric constant (ε_r)	Quality factor (Qxf GHz)	Temperature coefficient (τf:ppm/°C)
61	-	-	900	19.3	51200	-31
			925	22.5	84400	-29
62	0.25	-	900	23.6	50000	-23
			925	25.7	86100	-16
63	0.50	-	900	22.8	44000	-23
			925	25.5	77400	-13
64	1.00	-	900	22.4	46300	-15
			925	25.2	78000	+1
65	2.00	-	900	23.1	56600	0
			925	25.8	87600	-1
66	-	0.25	900	23.5	52000	-16
			925	25.3	84300	-15
67	-	0.50	900	23.6	46200	-6
			925	25.3	81700	-7
68	-	1.00	900	23.6	53700	-10
			925	25.2	79300	-5

69	-	2.00	900 925	24.5 26.1	56600 77200	-12 -7
70	-	5.00	900 925	16.5 25.1	40000 60200	-4 -4

In the embodiments 62~65 and 66~69, it is noted that the dielectric constant and the quality factor were higher when H3BO3 were added than B2O3, and especially, the stability of the temperature factor according to the sintering temperature was excellent, which testifies the effect of the present invention.

In the present invention, a high frequency dielectric ceramics composition may be constituted by combining a combination of $(Zn_{1-a}Mg_{1-b}Co_{1-c}Ni_{1-d})TiO_3$ and $yTiO_2$ as a main component and one of 0~5 wt % B_2O_3, 0~5 wt % H_3BO_3, 0~5 wt % SiO_2-K_2O glass, 0~5 wt % B_2O_3 and SiO_2-K_2O glass, or 0~5 wt % H_3BO_3 and SiO_2-K_2O glass as an additive, which satisfies conditions of $0\leq a\leq 1$, $0\leq b\leq 1$, $0\leq c\leq 1$, $0\leq d\leq 1$ and $0\leq y\leq 0.6$.

INDUSTRIAL APPLICABILITY

As so far described, a high frequency dielectric characteristic having an excellent various temperature compensation varied according to the high quality factor, the dielectric constant and the stable temperature coefficient and composition but having a very low sintering temperature compared with the conventional dielectric composition can be implemented at a low-priced

material such as ZnO, MgO, CoO, NiO or TiO_2.

In addition, since Ag, Cu or their alloy or Ag/Pd alloy can be used as an internal electrode, and thus, can be used as various high frequency devices, i.e., a multilayer chip capacitor, a multilayer chip filter, a multilayer chip capacitor/inductor composite device and a low-temperature sinterable substrate, a resonator and a filter or a ceramic antenna.

Especially, the low-temperature sintered composition obtains a remarkably high quality factor more than several times that of the conventional one.

In addition, combination of the almost infinite number of compositions exhibiting the excellent high frequency characteristic can be obtained in the composition range of the present invention.